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Tetramethyltetraselenafulvalene salts [$(TMTSF)_2X$]: Anisotropy and effective dimensionality of the Fermi surface

J. F. Kwak
Sandia National Laboratories, Albuquerque, New Mexico 87185
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With the use of an analytic approximation for the open Fermi surface of a system with highly anisotropic two-dimensional dispersion, it is shown that the plasma frequency anisotropy is linear in the bandwidth anisotropy. Comparison to the optical data on the Bechgaard salts of tetramethyltetraselenafulvalene [$(TMTSF)_2X$] implies a substantial transverse bandwidth of 140 meV, a full order of magnitude larger than previously supposed, and consistent with predominantly two-dimensional behavior. A critical discussion is presented of the model of, and supporting evidence for, large quasi-one-dimensional (1D) superconducting fluctuations. It is shown, using the above result, that there are several orders of magnitude discrepancy in the temperature obtained for crossover from 3D to 1D behavior. In addition the chief experimental results claimed as proof for fluctuations are susceptible to alternate interpretations.

The tetramethyltetraselenafulvalene [$(TMTSF)_2X$] series of organic compounds,[1] hereafter called the Bechgaard salts, continue to be of interest due to their novel electronic[1–5] and magnetic[6,7] properties, particularly the proposed competition[8] between superconductive[2,3] and spin-density wave[5–7] (SDW) instabilities. Except in the case of $X = ClO_4$, it has been necessary to apply pressure in order to attain superconductivity. This fact has led to a dichotomy in the field, with some work focused on the magnetic ground state at ambient pressure and some on the superconductivity. However, the possibility of coexistence of the two states[3,9] has gained increasing acceptance.[10,11] The high-field phase transition observed by NMR[12] and transport[4,13] studies appears to be related to this question. Most of the attention thus far has been attracted by the claims of Jerome and co-workers for quasi-one-dimensional (1D) superconductive fluctuations at temperatures as high as 40 K.[2,14,15] But the interpretations made in this context suffer from major inconsistencies and are in many cases directly contradicted by other experiments.[16,17]

In this paper it is shown that there is an order of magnitude larger transverse bandwidth in the Bechgaard salts, 140 meV, than previously supposed, consistent with predominantly 2D behavior. The band parameters are obtained from a comparison of the optical data[18] to the anisotropic plasma frequency derived for an open, 2D Fermi surface. It is seen that the simple analysis used by the authors of Ref. 18 in obtaining a small transverse bandwidth is inappropriate to the Bechgaard salts. The model of 1D superconductive fluctuations[15] is reviewed and seen to contain gross internal inconsistencies. In fact, based on the presently derived bandwidth, there is no region where fluctuation effects are significant. Finally, serious difficulties are seen to be associated with the interpretations made of various experiments in terms of the 1D model.

A proper derivation of the plasma frequency involves application of Lindhard's general expression for the dielectric function of an electron gas, and therefore requires some knowledge of the Fermi surface and electronic dispersion. We therefore begin by obtaining a simply analytic approximation for the open Fermi surface of a highly anisotropic 2D system. Consider a system with strong coupling (chains) along a and significant interchain coupling in only one transverse direction, b. We use the fairly general energy dispersion

$$E(\vec{k}) = E_a(\vec{k}\cdot\vec{a}) - 2t\cos(\vec{k}\cdot\vec{b}) \quad , \qquad (1)$$

where t is the interchain tight-binding coupling integral, and the a-axis dispersion E_a is left arbitrary. This should be a reasonable representation for the Bechgaard salts.[19] For simplicity of calculation the lattice is taken as orthorhombic, thus introducing errors on the order of $(1-|\vec{a}\times\vec{b}|)$ in quantities related to reciprocal space cross sections; this error is about 5% for the triclinic structure of the Bechgaard salts. The a and b components of the wave vector $\vec{k}$ can be described by the dimensionless variables $x \equiv \vec{k}\cdot\vec{a}$ and $y \equiv \vec{k}\cdot\vec{b}$, respectively. The Fermi surface, which becomes a pair of curves $\pm x_F(y)$ in this 2D system, is defined by (1) with $E(\vec{k})$ equal to the Fermi energy E_F. It is assumed that the Fermi surface is nearly flat,[20] with x_F deviating only a small amount δ from the $t=0$ constant value x_0, where x_0/π is the fractional band filling. Therefore, t must be small on some scale to be found *a posteriori*. Expanding E_a on the Fermi surface in a Taylor series about x_0 to second order in δ,

$$E_F = E_0 + E_0'\delta + E_0''\delta^2/2 - 2t\cos y \quad , \tag{2}$$

where $E_0 = E_a(x_0)$, etc.

We wish to obtain an expression for δ in terms of t. Holding the band filling constant as t is turned on requires $\int_{-\pi}^{\pi}\delta\, dy = 0$. Since $\delta \sim t$ to highest order, integration of (2) implies $E_F = E_0 + O(t^2)$. Solving (2) for δ via the quadratic formula and expanding to second order in t,

$$\delta = \frac{2t}{E_0'}\cos y + \frac{E_F - E_0}{E_0'} - 2\frac{E_0''}{E_0'^3}t^2\cos^2 y \quad . \tag{3}$$

The condition for validity of this result is $E_0' > 2t$, which should be satisfied sufficiently far from a band edge. Integrating (3) yields $E_F - E_0 = E_0''t^2/E_0'^2$, so

$$\delta = \frac{2t}{E_0'}\cos y - \frac{E_0''}{E_0'^3}t^2\cos 2y \quad . \tag{4}$$

Note that the shape of the Fermi surface depends on the derivatives on the Fermi surface of E_a, rather than directly on the bandwidth W_a—a result of the smallness of t.

Armed now with the simple approximation (4), it is easy to calculate the anisotropic plasma frequency $\omega_p(\hat{q})$, where $\hat{q}$ is the direction of light polarization. From Lindhard's expression in the limits $\omega(\vec{q}) \gg E(\vec{k}+\vec{q}) - E(\vec{k})$ and $T=0$,[21]

$$\omega_p^2(\vec{q}) = \left(\frac{e}{\pi\hbar}\right)^2 \int d^3k\,(\vec{q}\cdot\vec{\nabla}_k)^2 E(\vec{k}) \quad , \tag{5}$$

where the integral is restricted to filled states. If one were to assume a free-electron-like dispersion with anisotropic masses m_x and m_y and electron density n, one would immediately obtain

$$\omega_{px}^2 = 4\pi e^2 n/m_x, \quad \omega_{py}^2 = 4\pi e^2 n/m_y \tag{6}$$

as expected. However, a closed Fermi surface is implicitly contained in an effective mass dispersion, no matter how anisotropic, and the integral in (5) must be extended over as many zones as necessary to include all the occupied states. This procedure is clearly invalid for the open Fermi surface considered appropriate to the Bechgaard salts; it will be seen that serious errors are introducted by using (6) and identifying m_x and m_y with band masses.

We now proceed to evaluate (5) for a system described by (1) and (4). Note that for our system

$$\int d^3k \to \frac{2\pi}{V_c}\int_{-\pi}^{\pi} dy \int_{-(x_0+\delta)}^{(x_0+\delta)} dx \quad , \tag{7}$$

where $V_c = abc$ is the volume of a unit cell.

Case (i), $\hat{q} = \hat{x}$. Using $E_a(x) = E_a(-x)$,

$$\int dx \frac{\partial^2}{\partial x^2}E_a(x) \cong 2(E_0' + E_0''\delta + \tfrac{1}{2}E_0'''\delta^2) \quad . \tag{8}$$

Then, using (4) and (5),

$$\omega_{px}^2 = \frac{8e^2a^2}{\hbar^2 V_c}E_0'\left(1 + \frac{E_0'''}{E_0'^3}t^2\right) \tag{9}$$

to second order in t. The leading term in (9) is simply the result for a planar (1D) Fermi surface.[22] The correction term due to curvature will be assumed to be negligible in the discussion below. Note that ω_{px}^2 is related *not* to the band mass $(m^*)^{-1} \sim E_0'$, but to the Fermi velocity $\hbar V_F = aE_0'$.

Case (ii), $\hat{q} = \hat{y}$.

$$\frac{\partial^2}{\partial y^2}E(x,y) = 2tb^2\cos y \quad ,$$

and

$$\omega_{py}^2 = (16e^2b^2t^2/V_c\hbar^2E_0') + O(t^4) \quad . \tag{10}$$

Note that ω_{py}^2 goes at t^2, whereas applying (6) would have it to go as t. Thus it is in ω_{py}^2 that the small curvature of the Fermi surface is crucially important, contributing an extra factor of t. The anisotropy is

$$(\omega_{py}/\omega_{px})^2 = 2(bt/aE_0')^2 \quad . \tag{11}$$

The experimental values for the anisotropic plasma frequency, $\omega_{px} = 11\,400$ cm^{-1} and $\omega_{py} = 2360$ cm^{-1}, were obtained by Tanner *et al.*[18] from a Drude fit to the raw data on $(TMTSF)_2PF_6$. From (10), using $a = 7.3$ Å, we than have $E_0' = 0.25$ eV (corresponding to an a-axis Fermi velocity of 2.8×10^7 cm/sec). This result agrees remarkably well with the value predicted by the extended Huckel band calculation of Whangbo *et al.*[19] We can therefore confidently use our value for E_0' in (11), with $b = 7.7$ Å, to obtain $W_b = 4t = 0.14$ eV. Comparing this value to the widely quoted 0.013 eV obtained[18] from an incorrect analysis based on Eq. (6), the present estimate is a full order of magnitude larger. This result will be seen in the next section to be completely inconsistent with the model of large 1D fluctuation effects.

A notable feature of Ref. 22 is that the Fermi surface closes only for $W_b > 0.25$ eV, and hence should be open here. Models for the origin of the small closed orbits observed through the Shubnikov–de Haas effect[4] are discussed elsewhere,[8,23] where it is shown that the anisotropy results derived here are not significantly affected.

REVIEW OF 1D FLUCTUATIONS

A theoretical description of conductivity fluctuations in 1D superconductors, and its application to the Bechgaard salts, is given in a paper by Schulz *et al.*[15] It is in the latter discussion (cf. Sec. 4 of Ref. 15) that problems arise. The most serious of these is related to the degree of anisotropy as follows. A parameter "B" is introduced and treated as adjustable in fitting the data, although it is noted that formally $B = 2\pi^2 t^2/\Theta$, where the transverse coupling t is in degrees Kelvin; Θ is not defined in Ref. 17, but is seen by inspection to be $\hbar/k\tau$, where τ is the transport scattering time. Rather, the arbitrary value $B = 0.85$ K is used in fitting the a-axis resistivity of $(TMTSF)_2PF_6$. Although it is not stated in Ref. 17, the equations used in the fit are valid only for small $B < T_c$, the 3D ordering temperature, in which case there is a crossover from 3D to 1D behavior at $T^* = T_c + B$. In general, the crossover occurs when the transverse coherence length ξ is comparable to b, or $T^* \ln(T^*/T_c) = B$. Note that B is a measure of the effective dimensionality: Fluctuations are only important for *small B*. If B is large, 1D effects are not important and the 3D fluctuations are correspondingly reduced; indeed, the critical region is smallest for large B.

It will now be shown that any *reasonable* estimate for B is grossly inconsistent with the fitting value used by Schulz *et al.* Using $\Theta = 760$ K obtained from $\tau \sim 10^{-14}$ sec,[18] which is larger than the value 200 K used as a fitting parameter in Ref. 17, will tend to reduce B and hence favor 1D fluctuations. As noted above, the authors of Ref. 17 do not calculate B; however, they imply elsewhere in their paper that $t = 4$ meV (46 K) is a reasonable estimate. One then obtains $B > 50$ K, a value suggesting that 1D fluctuation effects are not very important. The fit to fluctuations is even worse if we use $t = 400$ K as found in the present paper; then $B \sim 4000$ K and $T^* \sim 620$ K. Not only are 1D effects never important, the 3D fluctuation conductivity is down by 1000 from that calculated in Ref. 17.

Another major discrepancy in Ref. 17 is the discussion of the a-axis conductivity anisotropy by their Eq. (4.3). This equation, presented without derivation, is used to fit the reported decrease in anisotropy below 40 K. But the fact is, as their Eq. (3.9) shows, the fluctuation anisotropy for $T > T_c$ will be *larger* than the single-particle (normal) value.

The discussion above indicates that the 1D fluctuation model *cannot* fit the measured conductivity of the Bechgaard salts, even remotely. What of other experimental evidence? The strongest claims for fluctuations are made on the basis of a large ($\sim$3 meV) gap observed by tunneling[24] and far ir[25] measurements, an apparent near-vanishing of tunnel junction resistance at 12 K for $(TMTSF)_2PF_6$ under pressure,[26] and heat-capacity measurements.[27] These experiments are considered in turn.

Both tunneling and far ir on the PF_6 and ClO_4 salts show a gaplike structure (pseudogap) at several millielectronvolts. It suffices here to say that these experiments have not shown the gap to be due to superconductivity. Indeed, the coexistence of SDW's and superconductivity mentioned in the introduction[3,9] would imply that the large gap is primarily due to SDW's.[28]

In another tunneling experiment,[26] the apparent contact resistance was found to decrease from 6 to 0.2 Ω below 30 K. This was interpreted as due to regions of "stabilized" superconductive fluctuations shorting the barrier. On the other hand, it is well known that even four-probe resistance, when measured in junction structures, includes a contribution from the electrodes.[29] It is also a fact that the resistance of the Bechgaard salts falls most rapidly precisely in the above temperature region. This effect, not addressed in Ref. 26, is the probable cause for the observed resistance drop.

Measurements of the heat capacity of the ClO_4 salt near T_c have been made and again interpreted in terms of 1D fluctuations.[27] A sharp anomaly is seen in zero magnetic field at $T_c \sim 1.2$ K, which is consistent with a gap almost perfectly BCS in magnitude (and inconsistent with fluctuations). But the authors of Ref. 27 discount this as "fortuitous," and draw the backward conclusion that because B (see discussion above) is small (in their estimation), the critical region is "narrow" so somehow the pseudogap is not seen! Data in a 63-kOe magnetic field are also presented and discussed in Ref. 27. There are two main points: (1) An apparent 70% enhancement of the electronic term, and (2) a broad anomaly centered at 1.4 K below which the electronic contribution is greatly decreased. Insufficient information was supplied to test the possible effect of addenda and lattice contributions on the supposed enhancement; nor were data reported at temperatures sufficiently removed from the anomaly to gauge its effect. The anomaly is interpreted as signaling a transition from a fluctuating superconductive state above 1.4 K to a semimetallic SDW state below. In fact, the density of states in the SDW phase should not be much changed from the original band value,[11] so this interpretation cannot be correct.

SUMMARY

It has been shown that a proper analysis for an open 2D Fermi surface yields a plasma frequency anisotropy linear in the transverse bandwidth. Applying this analysis to the optical data on $(TMTSF)_2PF_6$ yields $W_b \sim 140$ meV, a value much larger than previously supposed. The a-axis plasma frequency has been shown to be closely consistent with the band structure of Whangbo *et al.* These results are consistent with predominantly 2D behavior.

A review of the theoretical model for 1D superconducting fluctuations, as applied to the Bechgaard salts, has shown gross inconsistencies: there is nearly three orders of magnitude error in the 3D-to-1D crossover temperature—with the proper value such that 1D effects are negligible; and the conductivity anisotropy behavior actually predicted by the theory is opposite to that observed. Major flaws in the interpretation of various experiments purporting to support this scheme have been discussed.

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